Graphene and doped graphene from adsorbed molecules

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Chapter 1

Introduction

In this chapter we shall summarize the methods to grow graphene and doped graphene on metal surfaces and explain the importance of the molecular route to grow graphene followed in present study. At the end of this chapter an outline of this dissertation will be presented.

The curious nature of human beings constantly pushes them to go beyond new horizons in every aspect of life, thus triggering a sense to develop themselves and the societies they live in. Resources and materials played an important role in structuring the human civilization throughout history. Bronze and iron helped to shape the human history in such a way that they have entire eras named after them. With the rise of the industrial revolution, the struggle to search for new materials with improved properties became crucial for sustainable and fast progress and development. The twentieth century saw a huge breakthrough in the field of information technology when silicon semiconductors enabled the production of computers. These materials played a crucial role in modernising the human civilization. Material Science has been moving from 3 dimensional (3D) to 2D materials over the past decade as these planar solids have the potential to transform the future due to their small sizes and extraordinary properties. One such material is graphene that has surprised the scientific community with its outstanding properties. Andrei Geim and Konstantin Novoselov were awarded the Nobel Prize in Physics in 2010 for their discoveries concerning this material. Despite a lot of effort in the field still there is no reliable way to produce high quality graphene, which is upscalable for industrial use. This PhD project was conducted to get a better understanding of new methods for graphene growth and contribute to their further development to overcome present challenges faced by scientific community.

1.1 Graphene

Carbon (from Latin: *carbo* "coal" or “charcoal”) is the fifteenth most abundant element in the Earth's crust by mass, fourth in the universe after hydrogen,

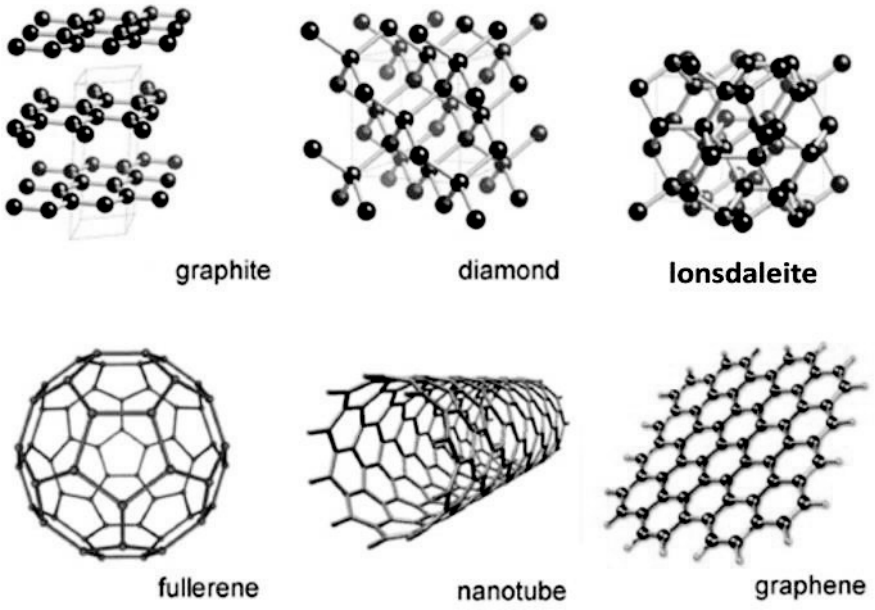

Figure 1.1: *Schematic representation of some allotropes of carbon*

helium and oxygen, and second in the human body (about 18.5%) after oxygen [1]. Carbon is one of the few elements known to humanity since ancient times [2] and crucial to the existence of life on earth. Carbon atoms can bind together in different ways to form allotropes like graphite, diamond, and amorphous carbon. The sp^3 hybridization gives rise to a tetrahedral lattice (diamond) while sp^2 leads to graphite. During the last few decades various new allotropes of carbon have been discovered, namely lonsdaleite [2], buckminsterfullerene (C_{60}) [3,4], carbon nanotubes (CNTs) [5], graphene [6] and Q-carbon [7]. Figure 1.1 shows the 3 crystalline allotropes of carbon, as well as the 3 low-dimensional allotropes.

Graphene is a two-dimensional network of sp^2-hybridized carbon atoms composed of two different triangular sub-lattices (A and B) arranged in a

hexagonal honeycomb. The first field effect transistor based on graphene obtained by micromechanical cleavage of graphite was reported by Andrei Geim's group in Manchester [6]. After these experimental studies the research interest in physics, chemistry and material science has been extensively focused on two dimensional carbon materials due to their interesting applications in nanotechnology [8,9,10]. Graphene shows exceptional electronic properties [6,11,12], it has a high tensile strength, mechanical stiffness [13], transport properties [12], unprecedented thermal conductivity [14] and is highly transparent for every wavelength of the light [15]. These properties have led to many suggestions for applications. The use of graphene has been proposed for sensors [16], gas separation membranes [17], supercapacitors [18], nanoelectronics [16], energy storage materials [19], transparent conductive coatings [20], biological filters [21], molecular sensors [22], transmission electron microscope supports [23,24] and nanocomposite materials [25,26].

Like semiconductors, also graphene can be chemically doped to tailor its properties. Usually two approaches are followed, either the graphene surface is modified by adsorption of individual gas molecules [17], metal atoms [27], or organic molecules [28], or the graphene lattice is substitutionally doped by introducing heteroatoms. Substitutional doping with atoms such as B, N, S and Si can locally induce significant changes in the electronic properties and chemical reactivity [29] of graphene. Boron or nitrogen doping the graphene network transform it into a p- or n-type semiconductor, respectively, accompanied by opening of a band gap [30]. n-doping is extremely significant for enhanced catalysis for energy conversion/storage [31–34]. The biocompatibility of carbon nanomaterials can also be enhanced by doping and doped graphene is therefore favourable for biosensing applications [34,35].

Graphene can be synthesized by different methods, *e.g.* by micromechanical cleavage [6] or chemical exfoliation [36] of graphite, by epitaxial growth [37] on metals and by chemical vapour deposition [38–41]. The most commonly used production method for graphene and doped graphene is chemical vapour deposition (CVD), where a hot metal substrate acting as a catalyst is exposed to hydrocarbons [40] or molecules containing also B and/or N (such as s-triazine $(HCN)_3$ [42] and hexaphenylborazine $(C_{36}H_{30}B_3N_3)$ [43]) and the desired 2D network is formed. In chemical vapour deposition, the growth starts at different points on the surface making defects and grain boundaries unavoidable. Since CVD proceeds at high temperatures, when the sample is cooled down to room temperature wrinkles develop due to the different thermal expansion coefficients of substrate and graphene. Preparing large continuous layers of graphene on conducting and insulating substrates is still a challenge. Another challenge is transfer of graphene without contamination to an insulating substrate for transport measurements. Using polymeric stamps and etching steps to eliminate the metallic substrate compromises the quality of graphene.

An alternative method to grow graphene is to start from self-assembled monolayers (SAMs) but this field has been little investigated so far. This approach will be part of this thesis. In the following we therefore introduce self-assembled monolayers and then explain graphene growth from SAMs.

1.2 Self-assembled monolayers

Self-assembled monolayers (SAMs) are ordered molecular assemblies formed by the adsorption of molecules on solid surfaces (Figure 2). The

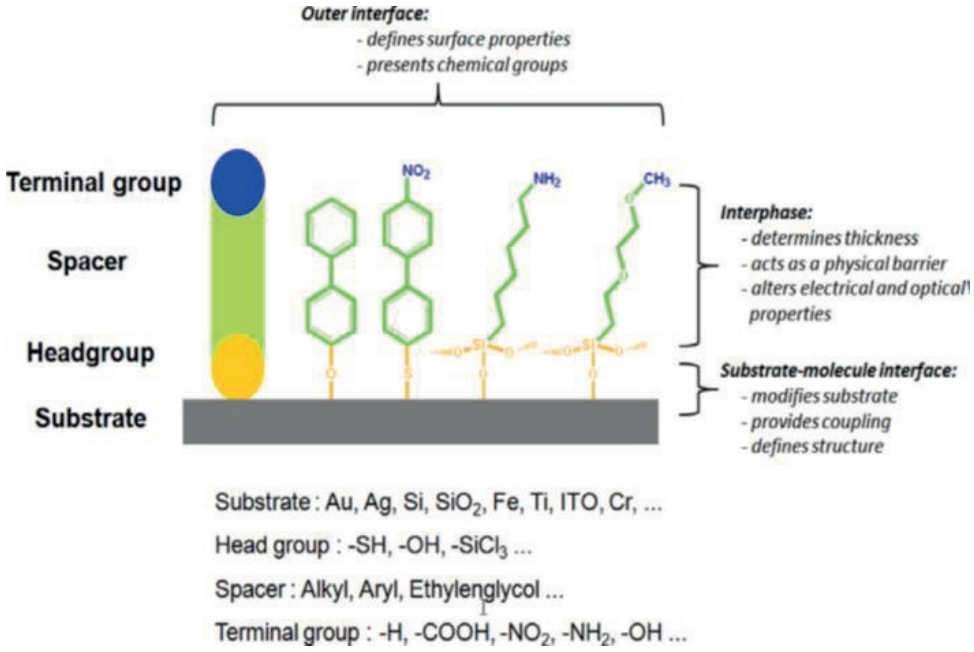

Figure 1.2: *Schematic representation of a self-assembled monolayer (SAM) showing different parts and their functions (Adapted from [72])*

preparation of self-assembled monolayers is easy and simple, thus making SAMs technologically attractive for surface engineering. A densely packed molecular monolayer is spontaneously formed within a few hours when a metallic substrate is immersed in a disulfide or thiol solution. In particular, the SH groups form covalent bonds with the surface upon hydrogen release [44–47] followed by lateral ordering driven by intermolecular interactions. The adsorption of fatty acids and alkyl silane molecules on Al_2O_3 and SiO_2 surfaces were studied by Sagiv [48,49]; he investigated electrical conduction of the self-assembled monolayers. This study is considered as a pioneering work in experimental molecular electronics. Nuzzo *et al*. [50] worked on self-assembly of bifunctional organic disulfides molecules thereby

trailblazing the research of thiolate SAMs on metals. The formation of self-assembled monolayers starting from different precursor molecules on metal, semiconductor and insulator substrates has been studied by various spectroscopic, microscopic and diffraction techniques [44,45],[61–71].

The molecules which arrange in SAMs typically consist of three building blocks: a head group forming a strong bond to a solid surface (substrate), a terminal group or end group that constitutes the outer surface of the SAM, and a spacer that connects head and terminal group (Figure 2). The intermolecular packing and the degree of order in the SAMs is controlled by spacer group and surface properties (hydrophilic or hydrophobic) by the terminal group. SAM can be formed on various types of substrates - metals, semiconductors and oxides.

SAMs can be used to control wetting and adhesion [8], improve chemical resistance or biocompatibility, serve as a sensitizer or a template for nanofabrication [44] affording applications in bioengineering, electrochemistry and electronics, as well as in nanoelectromechanical systems (NEMS) and microelectromechanical systems (MEMS).

1.3 Aromatic self-assembled monolayers (SAMs) and graphene growth

Rubinstein and co-workers introduced SAMs with aromatic spacer groups [53] that show a different packing density as compared to SAMs consisting of alkane spacers [58,73]. The properties of aromatic SAMs can be modified by the introduction of alkane groups between the aromatic spacers and head groups of the SAM building molecules [74]. The alkane spacers with even

number form more ordered SAMs with a higher packing density as compared to spacers with the odd number [75–78]. The possibility to tune the properties such as surface density and structure of aromatic SAMs can be useful in material science applications. The aromatic SAMs show interesting chemical and structural modifications when subject to electron, ion and photon irradiation.

When aromatic SAMs are irradiated with electrons or UV light, their bonds change. In brief, the three types of UV/electron induced modifications in are: (I) in aliphatic SAMs (alkane thiols) a cleavage of C–H bonds is induced by electrons that leads to desorption of material and formation of C=C double bonds in the fragments that remain on the surface. Aliphatic SAMs are used as positive tone resists in wet-chemical processes [79,80]. (II) In aromatic SAMs the irradiation induces C–H cleavage followed by crosslinking between neighbouring phenyl rings. Cross-linked phenyl rings maintain their preferred orientation and material desorption is minimum; hence the molecularly dense cross-linked monolayer obtained can be used as a negative tone electron resist [81,82]. (III) In aromatic SAM terminated with nitro groups, C–H cleavage also occurs, but hydrogen reduces the nitro to amino groups, which can be further chemically modified by electrophilic agents. Thus irradiation can be used to convert the terminal functionality, while the underlying aromatic layer is dehydrogenated and cross-linked.

In this dissertation, chapters three and four report on the growth of graphene/doped graphene starting from thermal decomposition of aromatic SAMs after irradiation with UV light. The crosslinking step is necessary because the temperatures necessary to transform the molecules into

graphene are higher than the desorption temperature of the non cross-linked molecules. This bottom up technique is simple and has the potential of being upscalable. Growing graphene by this method has several advantages; first, a self-assembled monolayer contains a well-defined amount of carbon; hence if the right molecules are chosen only one sheet of graphene is expected. Second, if the SAM is close-packed and covers the substrate surface uniformly, we anticipate growth of a continuous graphene layer avoiding many defects due to multiple nucleation sites typical for CVD-grown graphene. Moreover, by using molecules where one or more C atoms of the aromatic ring are replaced by B or N, it should be possible to obtain doped graphene with well-defined amounts of one or more heteroatoms (B, N, Al,..). Turchanin and coworkers [83] have shown that it is possible to obtain graphene on gold substrates from SAMs of biphenylthiol, which were first polymerized by electron irradiation and then heated in ultrahigh vacuum (UHV~10^{-10} mbar) to form the 2D carbon lattice.

Two chapters of this dissertation are devoted to a simpler method *i.e.* growing graphene by polymerizing SAMs with light and heating not in UHV. Moreover, copper foils were used instead of gold substrates because they are economically more viable. The grown material (graphene) was characterized with spectroscopic and microscopic techniques.

1.4 Outline of thesis

In this Ph.D. project "Graphene and doped graphene from adsorbed molecules" our aim was to synthesize large area graphene/doped graphene sheets from adsorbed molecules. The goal of this work was to investigate if

by such growth protocols graphene of comparable or even better quality than CVD-grown graphene could be obtained; whether the growth was possible also on insulating surfaces if the right molecules were chosen; and finally if it is possible to produce doped graphene by this molecular route. This dissertation is organized as follows:

Chapter 2, entitled *Experimental Section,* gives an overview of the methods used to synthesize graphene on Cu foils and Cu(111) by CVD. The experimental techniques employed to characterize the grown materials are also described briefly.

In Chapter 3, entitled *Graphene from biphenyl 4-thiol (BPT) molecules*, we present a molecular route for growing graphene on clean and oxidized Cu foil and describe how the quality of the grown material was verified with a variety of techniques.

In Chapter 4 we discuss the synthesis and characterization of *Doped graphene from polymerized self-assembled monolayers of borazine*. In particular we determined the ratio of hetero- to carbon atoms that can be obtained in the final product via this route to doped graphene.

Chapter 5, entitled *Graphene from* C_{60}, focuses on the growth of graphene on Cu(111) starting from chemisorbed molecules. Low energy electron diffraction, Raman spectroscopy and X-ray photoelectron spectroscopy were used to characterize the various intermediate products and the resulting graphene.

Chapter 6, with the title *Doped graphene from* $C_{59}N$ *molecules*, explores an alternative synthesis route of doped graphene. Also here the quality of the

final material was characterized by spectroscopic and microscopic techniques and compared to other production techniques.

Summary (English, Dutch & Urdu) and acknowledgements complete the thesis.

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